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Electronic Supporting Information (ESI)

Capturing the metastable state in the spontaneous and reversible Single-Crystal-to-Single-Crystal phase transition in riluzolium oxalate

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S-1: salt Preparation

Riluzole was obtained from Rallis India Limited. Oxalic acid was purchased from Sigma-Aldrich Company. The solvent drops grinding (SDG), also known as liquid-assisted grinding (using MeOH as solvent), was performed by mechanical grinding of riluzole and oxalic acid using agate mortar and pestle. Mechanical grinding was usually performed for a period of30 minutes with the dropwise addition of MeOH solvent, at an interval of 5 minutes each. The resulting powder was crystallized using HPLC grade MeOH solvent in 5ml beakers ata temperatureof 5°C.

S-2: Single Crystal X-ray Diffraction (SCXRD)

The single crystal X-ray diffraction measurements of RZ-OA salt crystal structures for all the temperatures (RZ-OA-270K (Form 1), RZ-OA-225K (metastable state), RZ-OA-190K (metastable state), RZ-OA-170K (metastable state), and RZ-OA-100K (Form 2)) were carried out on a Bruker APEX II Kappa CCD single crystal diffractometer equipped with a graphite monochromator using MoKα radiation (λ = 0.71073 Å) [1]. The multi-scan absorption correctionsof RA-OA salt were applied using SADABS [2]. The salt crystal structures were solved by direct methods using SIR92 [3] and refined with a full-matrix least-squares method using SHELXL-2016 [4] present in the program suite WinGX [5]. All non-hydrogen atoms of RA-OA salt were refined anisotropically. All the hydrogen atoms bound to carbon were placed in the calculated positions. However, all hydrogen atoms attached to the nitrogenfor all crystal structures (RZ-OA-270K, RZ-OA-225K, RZ-OA-190K, RZ-OA-170K, and RZ-OA-100K) were located from the difference Fourier map. DFIX was used for H2, H3B, and H5A hydrogen atoms bound to the nitrogen atom for RZ-OA-190K crystal data to restrain N-H distances at their targeted positions. The isotropic U-values of the hydrogen atoms to the nitrogen of 190 K and 100 K crystal data are the conventional fixed value of $1.2U_{eq}$ (N). However, the hydrogen atoms to the nitrogen of 170 K, 225 K, and 270 K crystal data no constrain was used for the isotropic U-values. The isotropic U-values of the hydrogen atoms to the carbon of all crystal data (270K, 225K, 190K, 170K, and 100K) are the fixed value of $1.2U_{eq}$ (C) using riding model. Amongst all the temperature RZ-OA crystal structures, it is observed that in RZ-OA-225K and RZ-OA-190K containing $–OCF_3$ group disorder. The $–OCF_3$ group disorder of each RZ ions were analyzed using the PART command in SHELXL-2016 and were refined for two independent positions. For refinement of 190K data in SHELXL-2016, SADI, SIMU, DELU, ISOR, and RIGU restraints were used for similarity on bond lengths, angles, and isotropic behavior. Thermal parameters were also constrained to be equal to the same atom fractions using EADP command. The data refinement of 190K data was performed with TWIN and BASF scale parameter against HKLF4 reflection file. After the final refinement, in the case of 190K data, the twin component ratio being 0.72:0.28. The packing diagrams of all temperatures RA-OA salt were generated using Mercury 3.6 software package [6]. The X-ray values were used for geometrical calculations (packing analysis and interaction table) which was performed by applying the HTAB command in SHELXL-2016.

The RZ-OA-190K single crystal data was also solved in $P2_1/c$ space group (Form I unit cell) with R1 = 0.0738 and number of refined reflections = 1841. However, the correct space group is *Cc*(Form II unit cell)for 190 K crystal data [R1 = 0.0802] with higher number of refined reflections (5165).The RZ-OA-225K single crystal data solved onlyin $P2_1/c$ space group (Form I unit cell).

S-3: Variable Temperature Powder X-Ray Diffraction (VTPXRD)

The observed stoichiometric ratio (2:1) as obtained from SCXRD, was used to reproduce the formation of bulk salt. The resulting powder of RZ-OA was used for variable temperature experimental powder X-ray diffraction experiments. The VTPXRD patterns of RA-OA salt were recorded on PANalytical Empyrean X-ray diffractometer with CuKα radiation (1.5406 Å) under liquid nitrogen flow. Bulk powder of RZ-OA sample was placed on a silica sample holder and measured by a continuous scan between 5 to 60° in 2θ with a step size of 0.013103° at different temperatures.

S-4: Geometry of the Bragg peaks in RZ-OA-190K single crystal X-ray diffraction data

The structures at 190 K re-refined using a domain-structure approach [9] in $P2_1/c$ space Group (Form I unit cell) with R1 (Reflections) = 0.0738 (1841). But the disorder ratio is analogous to*Cc* space group structure (Form II unit cell) for 190 K crystal data [R1 (Reflections) = 0.0802 (5165)]. This exercise had proved that the phase found at 190 K is metastable. The disordered state (metastable state) is stable at a particular range of temperature (~235 K to ~180 K).The low-temperature phase (~180 K to ~100 K) is always the more stable one at low-temperature in terms of Free energy, and the high-temperature phase (~298 K to ~235 K) is always the more stable one at high-temperature in terms of Free energy.

$$\begin{matrix} Form\ I \\ c = 11.7207\ \text{Å} \\ R1 = 0.0738 \end{matrix} \quad \begin{matrix} a = 9.5229\ \text{Å} \\ \beta = 101.215^\circ \\ wR2 = 0.1959 \end{matrix} \quad \begin{matrix} b = 10.1012\ \text{Å} \\ Space\ Group = P21/c \\ Reflections = 1841 \end{matrix} \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{matrix} Form\ II \\ c = 11.7215\ \text{Å} \\ R1 = 0.0802 \end{matrix} \quad \begin{matrix} a = 19.044\ \text{Å} \\ \beta = 101.207^\circ \\ wR2 = 0.2145 \end{matrix} \quad \begin{matrix} b = 20.209\ \text{Å} \\ Space\ Group = Cc \\ Reflections = 5165 \end{matrix}$$

$$The\ metric\ relationship\ between\ the\ Form\ I\ and\ Form\ II\ for\ RZ-OA-190K\ single\ crystal\ data$$

$$\leftrightarrow$$

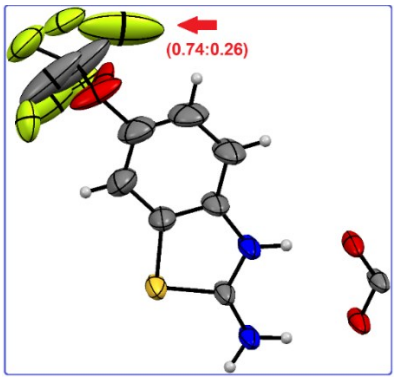
$$a^*/2(P2_1/c) = a^*(Cc)$$

$$b^*/2\ (P2_1/c) = b^*(Cc)$$

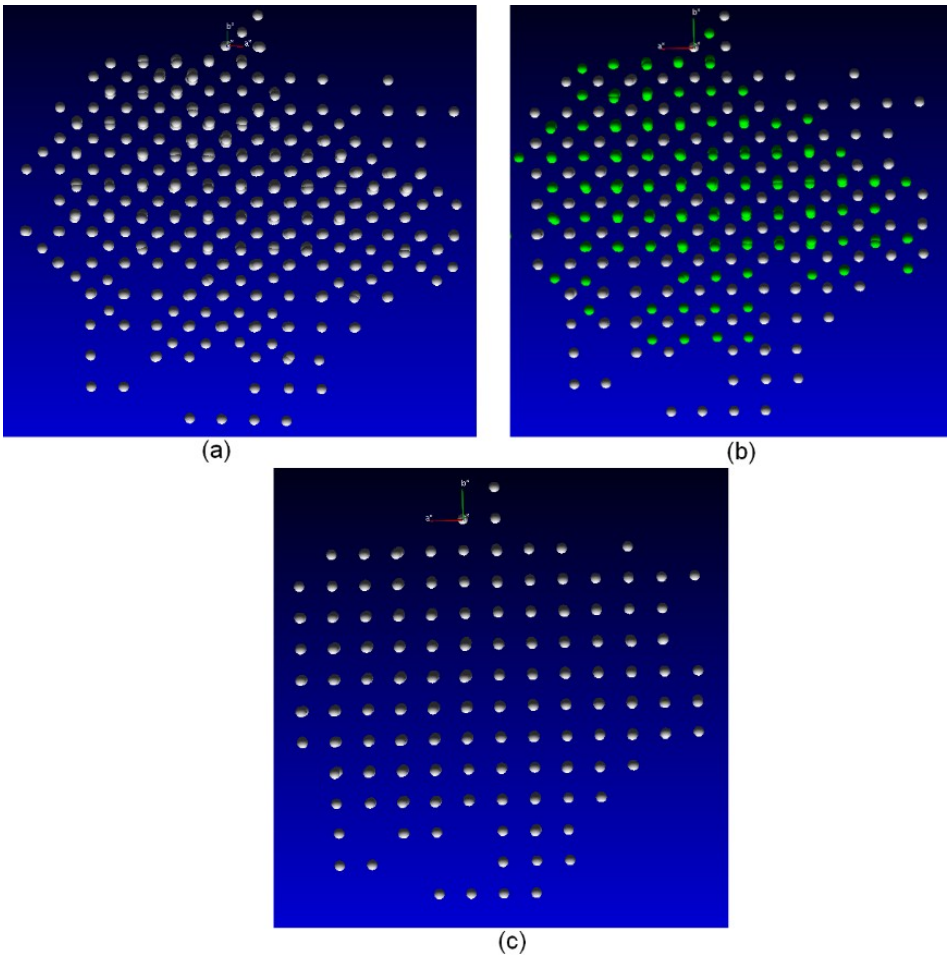
$$c^*(P2_1/c) = c^*(Cc)$$

$$\beta(P2_1/c) = \beta(Cc)$$

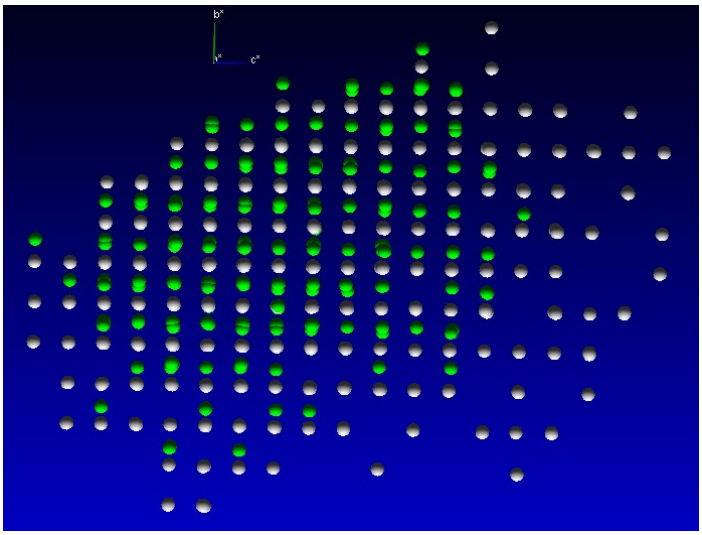
Since the lattice is monoclinic with identical c* and β in both cases, only the a* and b* directions of the diffraction patterns need to be described (after with ignoring any systematic absences). The reciprocal lattice for a general a*b* plane of the *Cc* structure (Form II) lies half-way between those of the $P2_1/c$ structure (Form I).



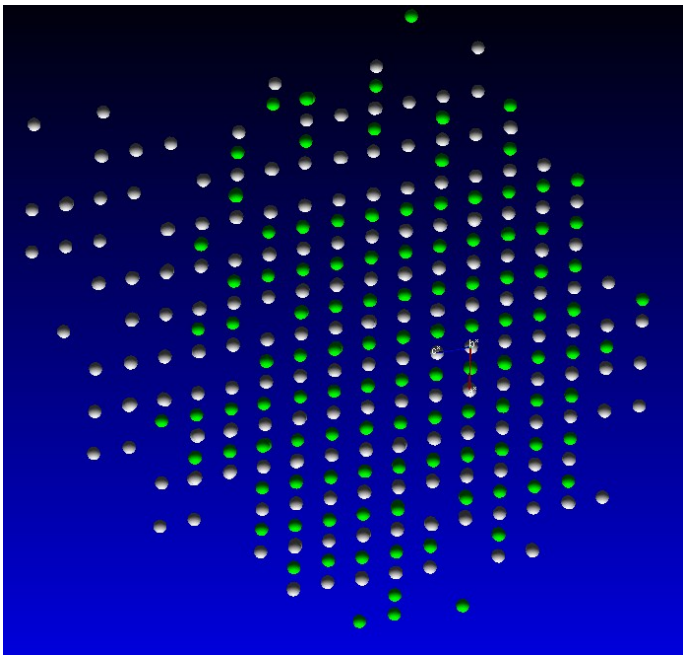
F-1: Asymmetric Unit of RZ-OA-190K solved in $P2_1/c$ Space Group (Form I unit cell) with R1(Reflections) = 0.0738(1841). Thermal ellipsoids @ 50% ellipsoidal probability. Significant changes in $–OCF_3$ group are shown with a red arrow.



F-2: The reciprocal lattice view of (a) RZ-OA-190K(*Cc*) [Form II unit cell] (gray colour reflections) in a*b* plane with I/σ = 5. (b) RZ-OA-190K($P2_1/c$) [Form I unit cell] (gray colour reflections) with removable reflections (green in colour) in a*b* plane with I/σ = 5. (c) RZ-OA-190K($P2_1/c$) (gray colour reflections) in a*b* plane with I/σ = 5.The number of such reflections to be removed is 274 out of 944 reflections.



(a)



(b)

F-3: The reciprocal lattice view of RZ-OA-190K($P2_1/c$) [Form I unit cell](gray colour reflections) with removable reflections (green in colour) with I/σ = 5 in (a) b*c* plane (b) a*c* plane. The number of such reflections to be removed is 274 out of 944 reflections.

References:

1. APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, 2006.
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T-1: Crystallography and refinement details

	RZ-OA-270K	RZ-OA-225K	RZ-OA-190K (*Cc*)
Stoichiometric ratio	1:0.5	1:0.5	4:2
Moiety formula (asymmetric unit)	$(C_8H_6F_3N_2O_1S_1^+)$, $0.5(C_2O_4^{2-})$	$(C_8H_6F_3N_2O_1S_1^+)$, $0.5(C_2O_4^{2-})$	$4(C_8H_6F_3N_2O_1S_1^+)$, $2(C_2O_4^{2-})$
Molecular formula	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$
CCDC	1572075	1572076	1572077
Formula weight	279.22	279.22	558.44
Temperature (K)	270(2)	225(2)	190(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	Cc
a (Å)	9.7557(4)	9.6547(5)	19.044(3)
b (Å)	10.0386(4)	10.0570(5)	20.209(2)
c (Å)	11.7809(4)	11.7482(5)	11.7215(14)
α (°)	90	90	90
β (°)	100.132(3)	100.553(4)	101.207(8)
γ (°)	90	90	90
Volume (Å^3)	1135.75(8)	1121.42(9)	4425.1(9)
Z, Z’	2, 0.5	2, 0.5	8, 2
Density (g/cm^3)	1.633	1.654	1.676
F (000)	564	564	2256
μ (mm^{-1})	0.328	0.332	0.336
θ (°) (min, max)	2.121, 29.626	3.779, 28.698	1.484, 24.999
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	(-13, 10), (-11, 13), (-16, 16)	(-12, 13), (-13, 11), (-15, 15)	(-22, 22), (-24, 24), (-13, 13)
Treatment of Hydrogen	mixed	mixed	mixed
No. unique ref./ obs. Ref.	3175/2055	2877/1983	7649/5165
No of parameters	175	239	786
R_all, R_obs	0.1072, 0.0753	0.0768, 0.0510	0.1165, 0.0802
wR_2_all, wR_2_obs	0.2453, 0.2204	0.1424, 0.1260	0.2591, 0.2145
$\Delta\rho_{min, max}$ (eÅ^{-3})	-0.446, 0.850	-0.328, 0.313	-0.487, 0.643
G.o.F	1.048	1.053	1.110

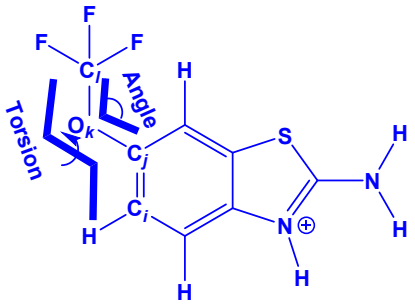
	RZ-OA-190K ($P2_1/c$)	RZ-OA-170K	RZ-OA-100K
Stoichiometric ratio	1:0.5	4:2	4:2
Moiety formula (asymmetric unit)	$(C_8H_6F_3N_2O_1S_1^+)$, $0.5(C_2O_4^{2-})$	$4(C_8H_6F_3N_2O_1S_1^+)$, $2(C_2O_4^{2-})$	$2(C_8H_6F_3N_2O_1S_1^+)$, $2(C_8H_5F_3N_2O_1S_1)$, $2(C_2H_1O_4^-)$
Molecular formula	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$	$2(C_8H_6F_3N_2O_1S_1^+)$, $(C_2O_4^{2-})$
CCDC	1828009	1572078	1572079
Formula weight	279.22	558.44	558.44
Temperature (K)	190(2)	170(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc	Cc

a (Å)	9.5229(13)	18.9397(12)	18.786(3)
b (Å)	10.1012(11)	20.1917(12)	20.184(3)
c (Å)	11.7207(14)	11.7038(7)	11.6566(17)
α (°)	90	90	90
β (°)	101.215(8)	101.450(3)	101.624(9)
γ (°)	90	90	90
Volume ($Å^3$)	1105.9(2)	4386.7(5)	4329.4(11)
Z, Z'	2, 0.5	8, 2	8, 2
Density (g/cm^3)	1.677	1.691	1.713
F (000)	564	2256	2256
μ (mm^{-1})	0.337	0.339	0.344
θ (°) (min, max)	2.684, 28.807	1.490, 30.247	2.494, 29.571
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	(-12, 12), (-13, 13), (-15, 15)	(-26, 25), (-27, 28), (-16, 16)	(-26, 25), (-23, 28), (-16, 14)
Treatment of Hydrogens	mixed	mixed	mixed
No. unique ref./obs. ref.	2868/1841	12083/9293	7045/3956
No of parameters	215	697	687
R_all, R_obs	0.1073, 0.0738	0.0705, 0.0485	0.1697, 0.0736
wR_2_all, wR_2_obs	0.2203, 0.1959	0.1336, 0.1192	0.1626, 0.1309
$\Delta\rho_{min, max}$ ($eÅ^{-3}$)	-0.560, 0.499	-0.412, 0.433	-0.495, 0.518
G.o.F	1.099	1.060	0.940

T-2: List of distances for proton shifting associated with atoms

N–H···O	**H···O distance (Å)**	**N···O**	**N···O distance (Å)**	**N–H**	**Bond distance (Å)**	**C=O/C–O**	**Bond distance (Å)**
RZ-OA-270K							
$N_2–H_2···O_3$	1.77(4)	$N_2···O_3$	2.603(3)	$N_2–H_2$	0.84(4)	$C_9–O_3$	1.258(3)
RZ-OA-225K							
$N_2–H_2···O_2$	1.62(3)	$N_2···O_2$	2.608(2)	$N_2–H_2$	0.99(3)	$C_9–O_2$	1.256(2)
RZ-OA-190K							
$N_2–H_2···O_{11}$	1.71(2)	$N_2···O_{11}$	2.610(14)	$N_2–H_2$	0.920(2)	$C_{35}–O_{11}$	1.27(2)
$N_6–H_6···O_5$	1.88(13)	$N_6···O_5$	2.633(13)	$N_6–H_6$	0.76(13)	$C_{10}–O_5$	1.27(2)
$N_4–H_4···O_9$	1.57(13)	$N_4···O_9$	2.596(16)	$N_4–H_4$	1.04(13)	$C_{36}–O_9$	1.25(2)
$N_8–H_8···O_2$	1.57(12)	$N_8···O_2$	2.623(15)	$N_8–H_8$	1.06(12)	$C_9–O_2$	1.25(2)
RZ-OA-170K							
$N_4–H_4···O_5$	1.74(5)	$N_4···O_5$	2.628(4)	$N_4–H_4$	0.90(5)	$C_{10}–O_5$	1.253(4)
$N_6–H_6···O_7$	1.74(6)	$N_6···O_7$	2.636(4)	$N_6–H_6$	0.90(6)	$C_{11}–O_7$	1.259(4)
$N_2–H_2···O_2$	1.60(7)	$N_2···O_2$	2.588(4)	$N_2–H_2$	1.01(7)	$C_9–O_2$	1.264(4)
$N_8–H_8···O_9$	1.47(6)	$N_8···O_9$	2.619(4)	$N_8–H_8$	1.14(6)	$C_{12}–O_9$	1.268(4)
RZ-OA-100K							
$N_2–H_2···O_5$	1.75(8)	$N_2···O_5$	2.648(8)	$N_2–H_2$	0.90(8)	$C_{10}–O_5$	1.254(9)
$N_8–H_8···O_9$	1.84(8)	$N_8···O_9$	2.631(8)	$N_8–H_8$	0.80(8)	$C_{20}–O_9$	1.258(9)
$N_4–H_4···O_8$	1.47(10)	$N_4···O_8$	2.570(8)	$N_4–H_4$	1.12(10)	$C_{19}–O_8$	1.272(9)
$N_6–H_6···O_3$	1.37 (8)	$N_6···O_3$	2.625(8)	$N_6–H_6$	1.26(8)	$C_9–O_3$	1.272(9)

T-3: List of torsion angles



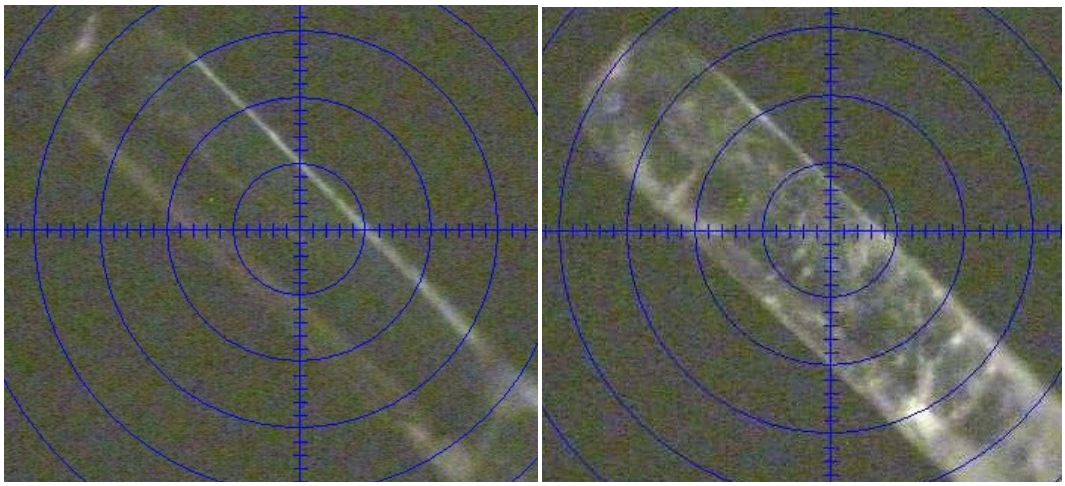
Compounds	Angle (C_j–O_k–C_l) (˚)	Torsion (C_i–C_j–O_k–C_l) (˚)
RZ-OA-270K	119.1(4) (C_5–O_1–C_8)	-89.7(8) (C_4–C_5–O_1–C_8)
RZ-OA-225K	118.2(7) (C_{5A}–O_{1A}–C_{8A})	81(1) (C_4–C_{5A}–O_{1A}–C_{8A})
RZ-OA-190K	123(2) (C_{5A}–O_{1A}–C_{8A})	-79(3) (C_{4A}–C_{5A}–O_{1A}–C_{8A})
	118(2) (C_{15}–O_{6A}–C_{18A})	98(3) (C_{14}–C_{15}–O_{6A}–C_{18A})
	110(1) (C_{23}–O_{7A}–C_{26A})	-86(3) (C_{22}–C_{23}–O_{7A}–C_{26A})
	130(2) (C_{31}–O_{8A}–C_{34A})	180(2) (C_{30}–C_{31}–O_{8A}–C_{34A})
RZ-OA-170K	116.7(3) (C_5–O_1–C_8)	-82.0(6) (C_4–C_5–O_1–C_8)
	117.0(4) (C_{17}–O_{10}–C_{20})	-84.6(6) (C_{16}–C_{17}–O_{10}–C_{20})
	120.9(4) (C_{25}–O_{11}–C_{28})	177.3(5) (C_{24}–C_{25}–O_{11}–C_{28})
	118.0(4) (C_{33}–O_{12}–C_{36})	81.4(6) (C_{32}–C_{33}–O_{12}–C_{36})
RZ-OA-100K	120.0(7) (C_5–O_1–C_8)	178.8(7) (C_4–C_5–O_1–C_8)
	116.7(6) (C_{15}–O_6–C_{18})	80(1) (C_{14}–C_{15}–O_6–C_{18})
	117.7(7) (C_{25}–O_{11}–C_{28})	-80(1) (C_{24}–C_{25}–O_{11}–C_{28})
	116.3(6) (C_{33}–O_{12}–C_{36})	-83.0(9) (C_{32}–C_{33}–O_{12}–C_{36})

T-4: Intermolecular interactions of RZ-OA salt at different temperatures.

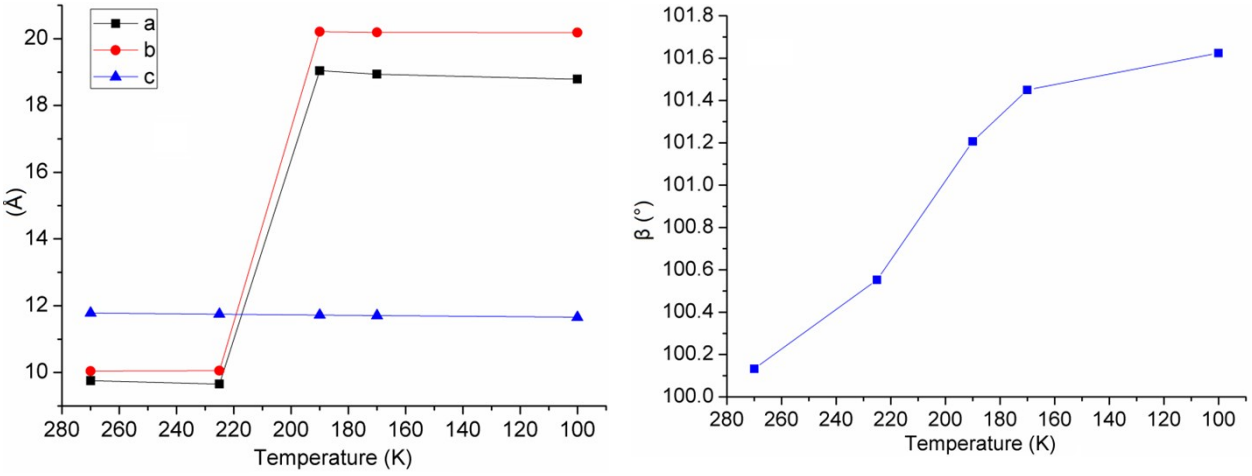
Motifs	Symmetry Code	Possible involved interactions	Geometry (Å/deg)
RZ-OA-270K			
I	x, y-1, z	N_1–H_{1B}···O_2 N_2–H_2···O_3	1.89(4), 164(3) 1.78(4), 169(4)
II	x, -y+1.5, z-1/2	N_1–H_{1A}···O_3 N_1–H_{1A}···O_2 O_2···S_1	2.05(4), 150(4) 2.43(4), 137(4) 2.968(3)
III	-x, y-1/2, -z+1.5	C_4–H_4···F_3	2.54, 147
IV	x, -y+1.5, z+1/2	O_1···S_1	3.135(4)
V	-x+1,-y+1,-z+1	C_1···C_2	3.386(4)
VI	-x+1,y-1/2,-z+1/2	N_1–H_{1B}···S_1	2.99(4), 124(3)
RZ-OA-225K			
I	-x+1, -y, -z+1	N_1–H_{1B}···O_3 N_2–H_2···O_2	1.87(3), 171(2) 1.62(3), 174(3)
II	-x+1, y+1/2, -z+1/2	N_1–H_{1A}···O_2 N_1–H_{1A}···O_3 O_3···S_1	2.04(3), 152(3) 2.45(3), 135(3) 2.954(2)
III	-x, +y+1/2, -z+1.5	C_4–H_4···F_{3A}	2.50, 144
IV	x, -y-1/2, z+1/2	O_{1A}···S_1	3.069(5)
V	-x+1, -y,-z+1	C_1···C_2	3.363(3)

VI	-x+1, y+1/2,-z+1/2	N_1–H_{1B}···S_1	3.04(3), 120(3)
RZ-OA-190K			
I(a)	x-1, y, z	N_1–H_{1A}···O_{12} N_2–H_2···O_{11}	2.07(14), 163(13) 1.71(2), 166(8)
I(b)	x-1/2, y+1/2, z	N_3–H_{3A}···O_{10} N_4–H_4···O_9	1.85(13), 160(11) 1.57(13), 171(12)
I(c)	x, y, z	N_5–H_{5A}···O_4 N_6–H_6···O_5	2.20(6), 124(6) 1.88(13), 169(14)
I(d)	x+1/2, y+1/2, z	N_7–H_{7A}···O_3 N_8–H_8···O_2	1.96(14), 172(12) 1.57(12), 169(11)
II(a)	x-1, -y+1, z+1/2	N_1–H_{1B}···O_{10} N_1–H_{1B}···O_{11} S_1···O_{10}	2.37(13), 134(10) 1.92(12), 150(11) 2.947(11)
II(b)	x, -y+1, z-1/2	N_3–H_{3B}···O_2 N_3–H_{3B}···O_4 S_2···O_4	1.96(4), 158(9) 2.44(8), 127(8) 2.938(10)
II(c)	x, -y+1, z+1/2	N_5–H_{5B}···O_3 N_5–H_{5B}···O_5 S_3···O_3	2.25(12), 145(10) 2.06(12), 126(9) 2.965(11)
II(d)	x, -y+1, z-1/2	N_7–H_{7B}···O_9 N_7–H_{7B}···O_{12} S_4···O_{12}	2.12(12), 126(10) 2.85(12), 97(8) 2.933(11)
III(a)	x+1/2, -y+1.5, z+1/2	C_{30}–H_{30}···F_{3A}	2.50, 128
III(b)	x, -y+1, z-1/2	C_{4A}–H_{4A1}···F_{4A}	2.56, 162
III(c)	x-1/2, -y+1.5, z+1/2	C_{14}–H_{14}···F_{7A}	2.63, 149
III(d)	x, -y+1, z-1/2	C_{22}–H_{22}···F_{11A}	2.61, 151
IV(a)	x+1/2, -y+1.5, z-1/2	O_{7A}···S_1	3.072(15)
IV(b)	x, -y+1, z+1/2	O_{6A}···S_2	3.10(2)
IV(c)	x-1/2, -y+1.5, z-1/2	O_{1A}···S_3	3.053(17)
IV(d)	x, -y+1, z+1/2	O_{8A}···S_4	3.66(2)
V(a)	x-1, y, z	C_1···C_{28} C_2···C_{27}	3.33(2) 3.32(2)
V(b)	x, y, z	C_{11}···C_{20} C_{12}···C_{19}	3.37(2) 3.35(2)
VI(a)	x+1/2, -y+1.5, z-1/2	N_3–H_{3A}···S_1	3.07(12), 113(8)
VI(b)	x, -y+1, z+1/2	N_5–H_{5A}···S_2	2.92(8), 127(8)
VI(c)	x+1/2, -y+1.5, z-1/2	N_7–H_{7A}···S_3	3.24(13), 116(10)
VI(d)	x-1, -y+1, z+1/2	N_1–H_{1A}···S_4	3.13(13), 131(11)
RZ-OA-170K			
I(a)	x, -y, z+1/2	N_1–H_{1A}···O_3 N_2–H_2···O_2	1.90(6), 167(4) 1.60(7), 166(6)
I(b)	x, y, z	N_3–H_{3A}···O_4 N_4–H_4···O_5	1.89(5), 164(4) 1.74(5), 172(5)
I(c)	x, y, z	N_5–H_{5A}···O_6 N_6–H_6···O_7	2.02(5), 174(5) 1.74(6), 174(5)
I(d)	x, -y+1, z-1/2	N_7–H_{7B}···O_8 N_8–H_8···O_9	1.85(6), 166(5) 1.47(6), 179(5)
II(a)	x, y, z+1	N_1–H_{1B}···O_4 N_1–H_{1B}···O_2 S_1···O_4	2.58(5), 137(4) 2.13(4), 152(5) 2.965(3)
II(b)	x, y, z-1	N_3–H_{3B}···O_7 N_3–H_{3B}···O_8 S_2···O_8	1.95(5), 135(4) 2.09(5), 140(4) 2.921(3)
II(c)	x, y, z	N_5–H_{5B}···O_3 N_5–H_{5B}···O_5 S_3···O_3	2.28(5), 139(4) 1.95(5), 142(4) 2.911(3)
II(d)	x, y, z	N_7–H_{7A}···O_9	2.05(4), 157(5)

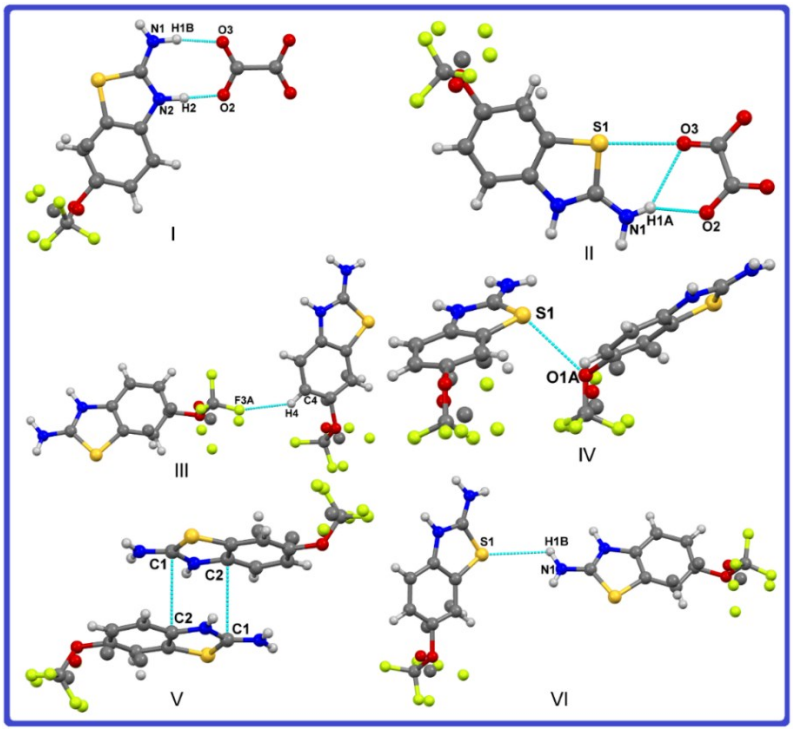
		N_7–H_{7A}···O_6 S_4···O_6	2.66(5), 132(4) 2.995(3)
III(a)	x-1/2, -y+1/2, +z+1/2	C_{24}–H_{24}···F_3	2.54, 128
III(b)	x+1/2, y-1/2,z	C_4–H_{4A}···F_6	2.50, 163
III(c)	x+1/2, y+1/2, z-1	C_{32}–H_{32}···F_8	2.58, 149
III(d)	x-1/2, -y+1/2, +z+1/2	C_{16}–H_{16}···F_{12}	2.57, 144
IV(a)	x, y, z-1	O_{12}···S_1	3.112(3)
IV(b)	x, -y+1, z+1/2	O_{10}···S_2	3.195(3)
IV(c)	x, -y, z+1/2	O_{11}···S_3	3.492(4)
IV(d)	x, y, z	O_1···S_4	3.012(3)
V(a)	x, y, z	C_1···C_{22} C_2···C_{21}	3.321(6) 3.292(5)
V(b)	x, y, z	C_{14}···C_{29} C_{13}···C_{30}	3.356(5) 3.362(5)
VI(a)	x, -y, z+1/2	N_1–H_{1A}···S_3	3.02(5), 124(3)
VI(b)	x, y, z-1	N_3–H_{3A}···S_1	3.05(5), 121(3)
VI(c)	x, y, z	N_5–H_{5A}···S_4	3.30(5), 120(4)
VI(d)	x, -y+1, z+1/2	N_7–H_{7B}···S_2	2.83(5), 120(4)
RZ-OA-100K			
I(a)	x, y, z	N_1–H_{1B}···O_4 N_2–H_2···O_5	1.92(9), 167(8) 1.75(8), 176(8)
I(b)	x, y, z	N_3–H_{3A}···O_7 N_4–H_4···O_8	1.90(9), 162(8) 1.47(10), 165(9)
I(c)	x, y, z	N_5–H_{5A}···O_2 N_6–H_6···O_3	1.91(9), 168(8) 1.37(8), 180(7)
I(d)	x, y, z	N_7–H_{7A}···O_{10} N_8–H_8···O_9	2.03(9), 169(10) 1.84(8), 166(9)
II(a)	x, y, z	N_1–H_{1A}···O_9 N_1–H_{1A}···O_7 S_1···O_7	2.05(8), 140(7) 2.32(9), 141(7) 2.885(7)
II(b)	+x, -y, +z+1/2	N_3–H_{3B}···O_8 N_3–H_{3B}···O_{10} S_2···O_{10}	2.10(8), 137(8) 2.44(9), 143(8) 2.937(7)
II(c)	+x, -y+1, +z+1/2	N_5–H_{5B}···O_3 N_5–H_{5B}···O_4 S_3···O_4	2.07(8), 139(8) 2.51(9), 140(7) 2.970(6)
II(d)	x, y, z-1	N_7–H_{7B}···O_5 N_7–H_{7B}···O_2 S_4···O_2	1.96(8), 154(7) 2.33(9), 127(6) 2.895(6)
III(a)	x+1/2, -y+1/2, +z-1/2	C_{24}–H_{24}···F_1	2.55, 149
III(b)	x-1/2, y+1/2, +z+1	C_4–H_{4A}···F_5	2.52, 128
III(c)	x-1/2, y-1/2, +z	C_{32}–H_{32}···F_9	2.58, 143
III(d)	x+1/2, -y+1/2, +z-1/2	C_{14}–H_{14}···F_{10}	2.49, 167
IV(a)	x, -y, +z+1/2	O_1···S_1	3.474(6)
IV(b)	x, +y-1, +z-1	O_6···S_3	3.007(6)
IV(c)	x, +y+1, +z	O_{11}···S_2	3.089(6)
IV(d)	x, -y+1, +z+1/2	O_{12}···S_4	3.207(5)
V(a)	x, -y, +z-1/2	C_{12}···C_1 C_{11}···C_2	3.302(11) 3.290(10)
V(b)	x, -y+1, z+1/2	C_{22}···C_{29} C_{21}···C_{30}	3.336(10) 3.331(10)
VI(a)	x, -y+1, +z-1/2	N_1–H_{1B}···S_3	3.19(9), 124(7)
VI(b)	x, y, z	N_3–H_{3A}···S_1	2.95(9), 129(6)
VI(c)	x, y, z+1	N_5–H_{5A}···S_4	2.86(9), 118(6)
VI(d)	x, -y, z-1/2	N_7–H_{7A}···S_2	3.14(9), 122(8)



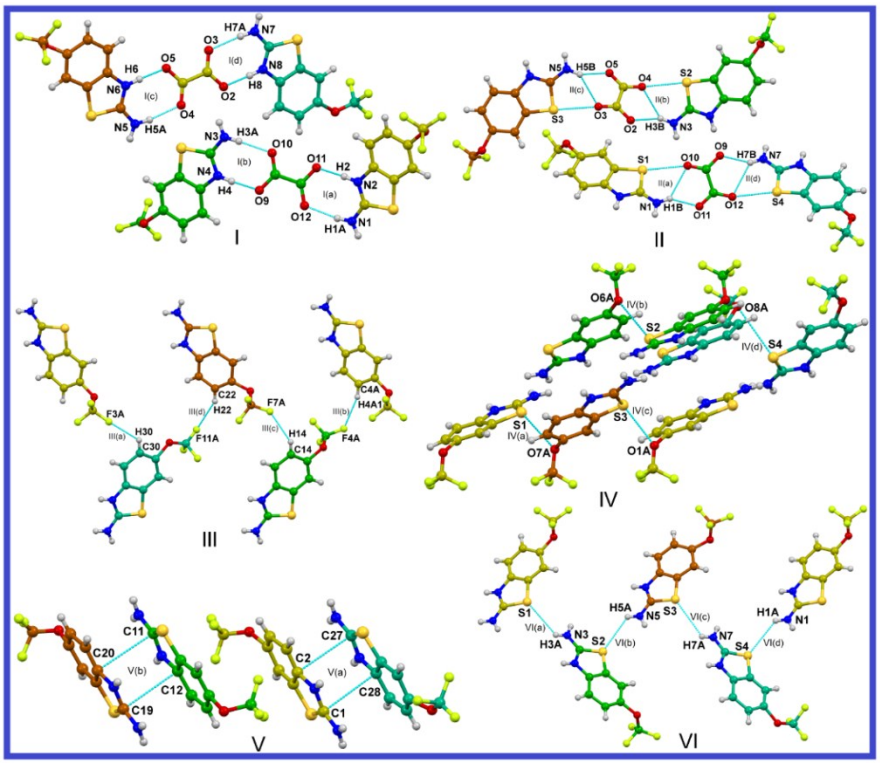
F-4: Crystal images of RZ-OA salt before [at 270 K temperature(left)] and after [at 100 K temperature(right)] SCSC transition.



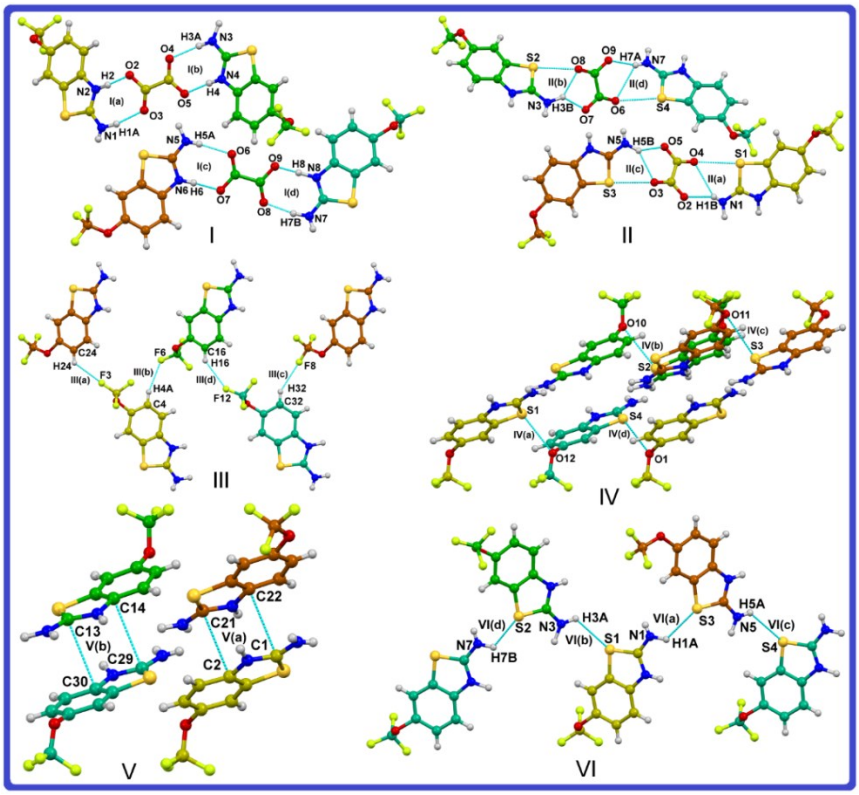
F-5: Variation in lattice parameters as a function of temperature.



(a) RZ-OA-225K



(b) RZ-OA-190K

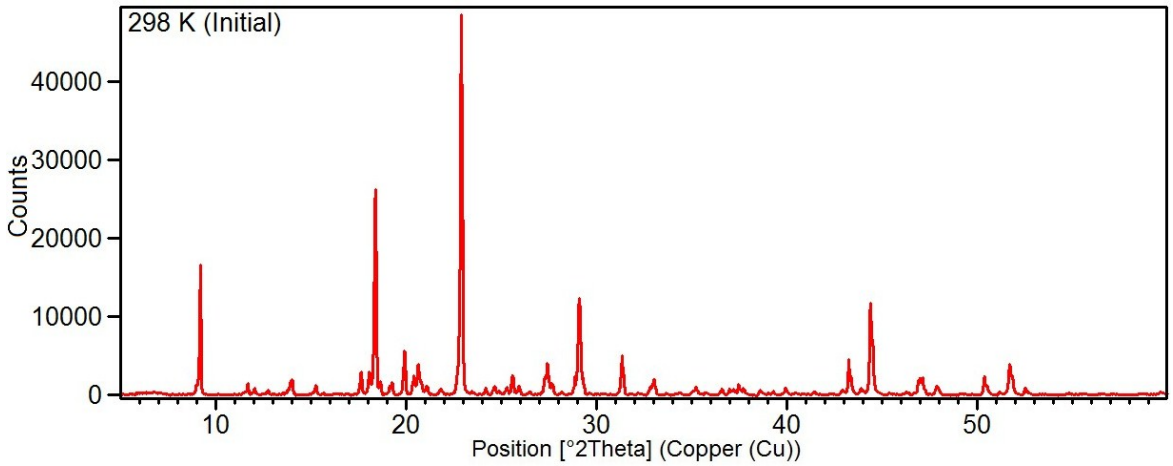


(c) RZ-OA-170K

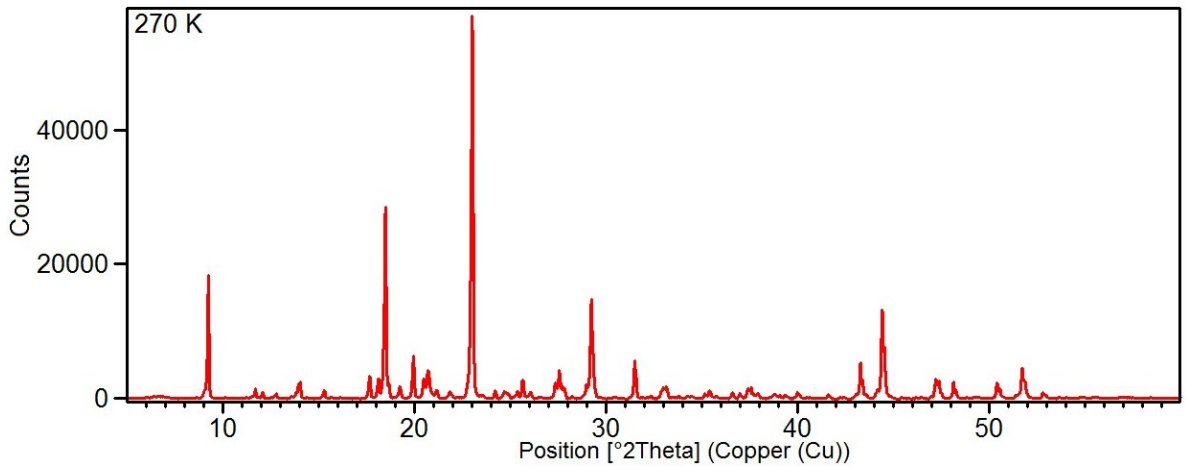
F-6: Molecular motifs representing key intermolecular interactions of RZ-OA salt at different temperatures. (a) 225 K (b) 190 K (c) 170 K. The non-bonded atoms represent disorder.

F-7: PXRD diagram of the RZ-OA salt.

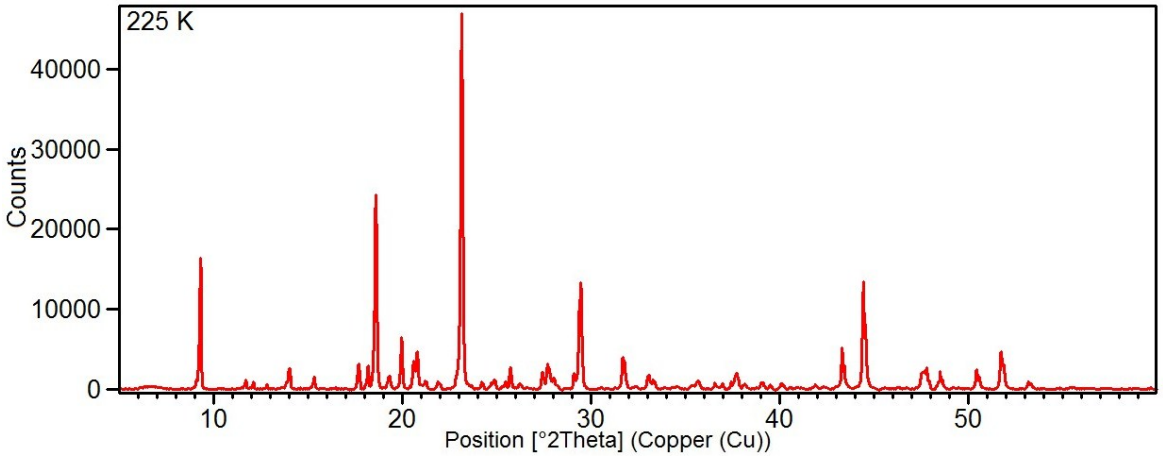
1. Experimental PXRD diagram at 298 K temperature



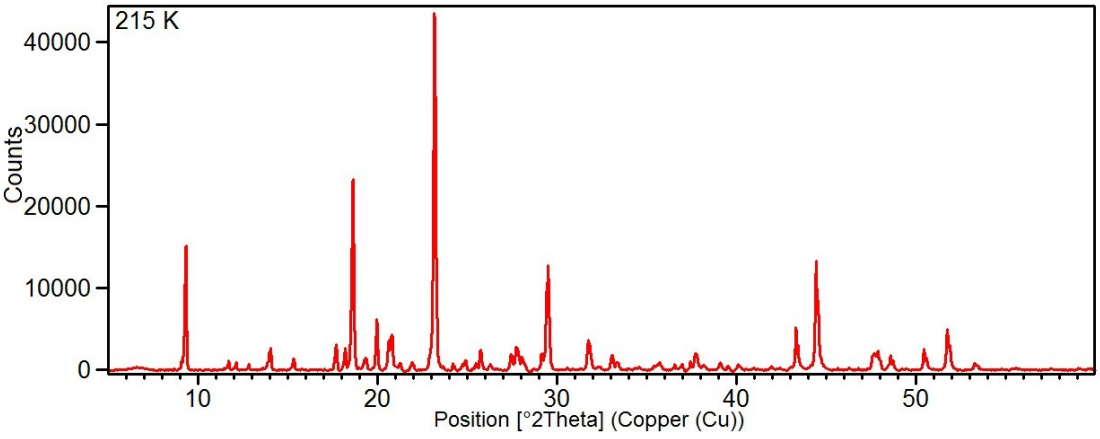
2. Experimental PXRD diagram at 270 K temperature



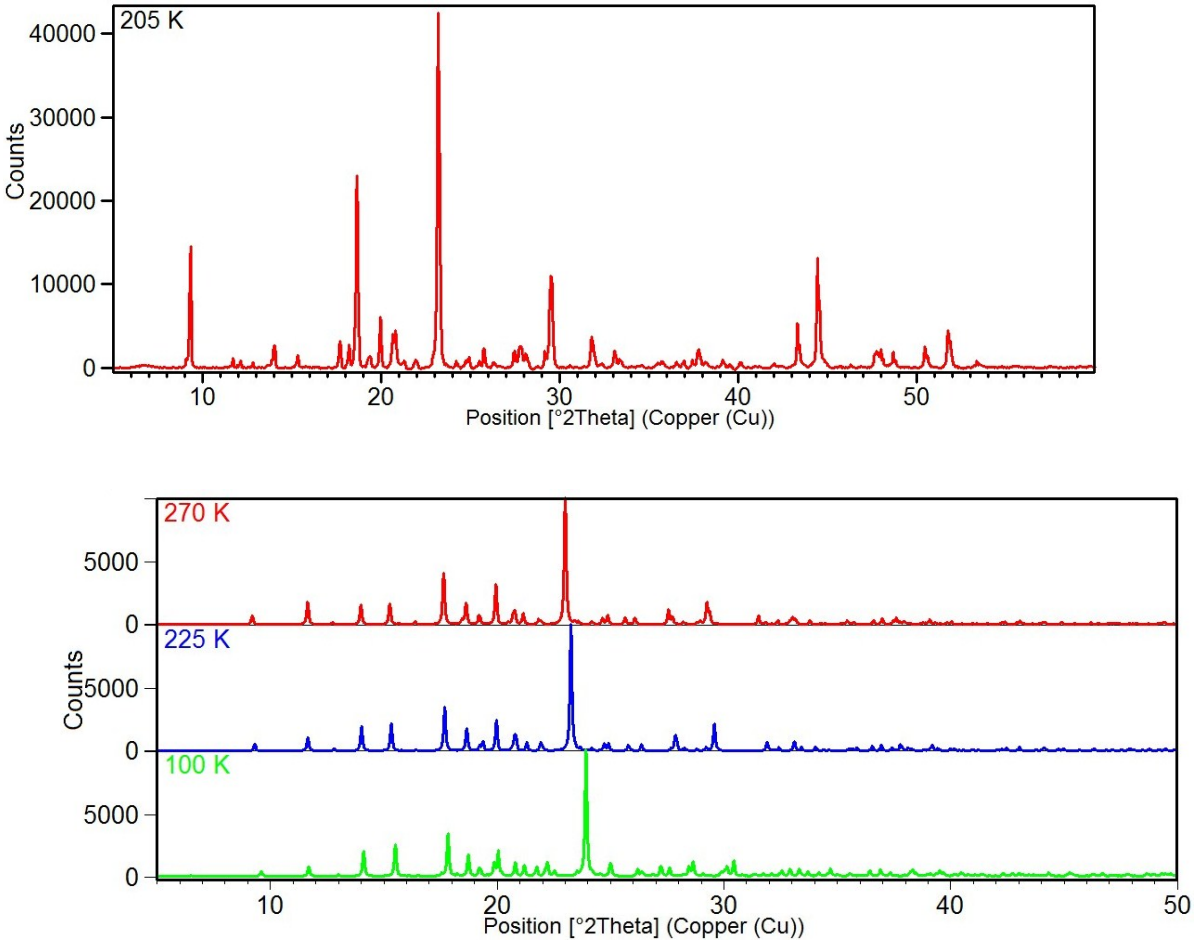
3. Experimental PXRD diagram at 225 K temperature



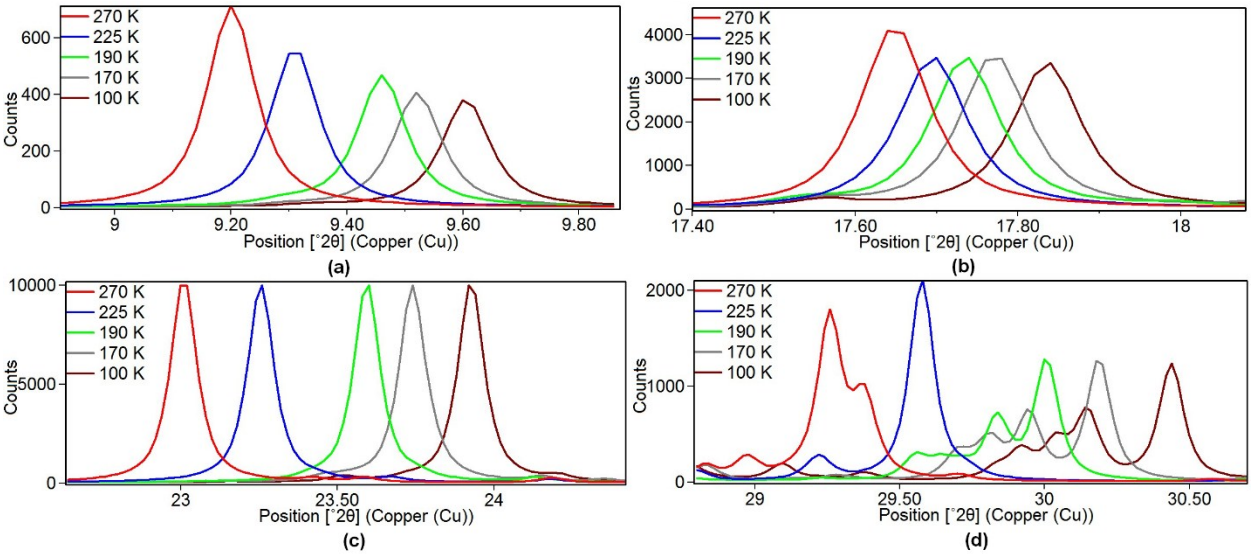
4. Experimental PXRD diagram at 215 K temperature



5. Experimental PXRD diagram at 205 K temperature



F-8: Simulated PXRD overlay diagram of RZ-OA salt at 270 K, 225 K, and 100 K.



F-9: Simulated PXRD peak overlay diagrams of RZ-OA salt at 270 K, 225 K,190 K, 170 K, and 100 K for (a) 9˚, (b) 18˚, (c) 23˚, and (d) 29˚.